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# CALCULATION OF NEAR-FIELD CONCENTRATIONS OF HYDROGEN SULPHIDE

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# CALCULATION OF NEAR-FIELD CONCENTRATIONS OF HYDROGEN SULPHIDE


## ABSTRACT

This report provides simulations of the near-field dispersion in the atmosphere of postulated releases of hydrogen sulphide gas (H2S) at a heavy water plant. The size and extent of the flammable or detonable gas clouds which might result are estimated. This work was undertaken to support experimental studies of the detonability of H2S releases.

Thirty-six different cases were simulated involving the catastrophic failure of a liquid H2S storage tank or tank car of H2S. The major variables were the size of the release, the initial mixing ratio of gas with ambient air, and the wind speed. Since the gas/air mixture is initially heavier than air, an existing heavy gas mathematical model (DENZ) was used for these simulations. The model was modified to provide the outputs needed to support the experimental studies. The outputs were the mass of H2S in the cloud, the mass and volume of the cloud, its radius at ground level and its temperature, all as functions of distance and time from release. The edge of the cloud was defined by a given concentration of H2S in air. The simulations were repeated for ten different values of this parameter, ranging between 3% and 40% H2S by volume.

Simulations were also performed using a simple "top-hat" mixing model to predict the length of the flammable or detonable jet formed at the break in a pipe carrying H2S vapour under pressure. The analysis was conducted for four postulated pipe break diameters and repeated for the same ten concentration levels used in the storage tank studies.

The report presents a summary of the results. The complete outputs from the 36 storage tank faiulure simulations are available on floppy disks in a format suitable for detailed examination using any IBM-PC compatible microcomputer system.



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## RÉSUMÉ

Le présent rapport fournit des simulations de dispersion rapprochée de rejets hypothétiques d'hydrogène sulfuré ($H_2S$ gazeux) dans l'air en provenance d'une usine d'eau lourde. Il donne également un calcul estimatif de la taille et de l'étendue des nuages inflammables et détonnants de ce gaz qui pourraient se produire. Le travail a été effectué à l'appui des études expérimentales sur la détonabilité des rejets d'hydrogène sulfuré.

On a simulé 36 cas de défaillances catastrophiques dans un réservoir de stockage d'acide sulfhydrique ($H_2S$ liquide) ou dans un camion-citerne d'acide sulfhydrique. Les variables principales tenaient à la taille du rejet, au ratio de mélange initial du gaz et de l'air ambiant, ainsi qu'à la vitesse du vent. Comme le mélange de gaz et d'air est plus lourd que l'air au départ, on s'est servi d'un modèle mathématique existant de gaz lourd (DENZ) pour ces simulations. Le modèle a été modifié pour fournir des données nécessaires à l'appui des études expérimentales. Les données comprenaient le poids d'hydrogène sulfuré dans l'air, le poids et le volume du nuage, son rayon au sol et sa température, le tout comme fonctions de la distance et du temps depuis le rejet. Le bord du nuage a été défini par une concentration donnée d'hydrogène sulfuré dans l'air. Les simulations ont été répétées avec dix valeurs différentes de ce paramètre, variant entre 3 % et 40 % d'hydrogène sulfuré par volume.

Des simulations ont également été effectuées en utilisant un simple modèle de mélange cylindrique pour prévoir la longueur du jet inflammable ou détonant qui se forme au point de fissure d'un tuyau d'hydrogène sulfuré sous pression. L'analyse a porté sur quatre diamètres différents de fissure de tuyaux et reprise pour les mêmes dix niveaux de concentration des études sur les réservoirs de stockage.

Le rapport présente un résumé des résultats. Les données complètes des 36 simulations de défaillances de réservoir de stockage sont disponibles sur disquettes flexibles dans une présentation appropriée pour en faire l'examen détaillé à partir de tout système informatique compatible avec l'appareil IBM-PC.

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## A. INTRODUCTION

The work described in this report is concerned with the initial, near-field dispersion in the atmosphere of postulated releases of hydrogen sulphide gas ($H_2S$) at a heavy water plant and the prediction of the size and extent of flammable or detonable clouds which might result. The work was undertaken to support the design of an experimental study of the detonability of $H_2S$ releases to be carried out for the Atomic Energy Control Board by the Defence Research Establishment, Suffield.

The specific scope of work included the use of an existing computer code (DENZ) to predict the dispersion of the heavier-than-air cloud which would result from the catastrophic failure of a storage tank or tank car of $H_2S$. The code was modified to provide the needed outputs of cloud radius, mass and temperature as functions of time and distance from the point of release, with the edge of the cloud defined by a specified concentration of $H_2S$. The modified code was then run for 36 combinations of the major input parameters, i.e., the mass of $H_2S$ released, the initial mass ratio of air to $H_2S$ and the wind speed. A second element of the work involved the use of a simple "top-hat" mixing model to predict the length of jet formed at the break in a pipe carrying $H_2S$ vapour under pressure. As with the cloud, the extent of the jet was defined by a specified concentration of $H_2S$. This analysis was carried out for four postulated pipe break diameters.

The following chapters of this report provide further details of the mathematical models and input parameters employed (Chapter B), the results of the analyses, including tabulations of the major output parameters and sample plots illustrating the $H_2S$ cloud behaviour (Chapter C). A discussion of these results is included in Chapter C. The conclusion of the report is found in Chapter D.

## B. MODELLING METHODOLOGY

Two separate mathematical models were used in this study to represent, in one case, the dispersion of the releases from a storage tank or tank car rupture and, in the other case, the dispersion of the release from a pipe break.

### 1. Storage Tank and Tank Car Rupture

The catastrophic failure of a storage tank or tank car of liquid H2S would result in the almost immediate formation of a cloud of H2S vapour mixed with ambient air which would initially be heavier than air. It has been observed experimentally that such a dense cloud then undergoes gravitational slumping, i.e., it simply flattens out, gradually entrains ambient air at its edges, but at a rate slower than would be the case for a passive cloud, and eventually transforms to a passive cloud which entrains air at the normal rate determined by the prevailing levels of atmospheric turbulence. A computer code specifically designed to describe this behaviour for the release of toxic or hazardous gases was developed by the U.K. Atomic Energy Authority. This code (DENZ) was subsequently obtained by the Atomic Energy Control Board and implemented by Monserco Limited on the firm's DEC VAX 11/750 computer in the course of a previous study for the Board (Ref. 1). DENZ was used again in the present work.

DENZ has been classified as a "slab" model (Ref. 2) which assumes a cylindrical shape of the cloud. Mass transfer occurs across the edges of the cloud by entrainment and mixing within the cloud is assumed to be sufficiently rapid for there to be a uniform concentration. The effects of heating of the cloud by the ground can be treated by the model but has not been included in this study. Transition to a passive cloud is assumed to occur when the rate of entrainment of air reaches a certain level

or when difference between the cloud and the ambient air becomes less than a specified value (0.001 kg/m³). For the purposes of calculating the concentrations of toxic or explosive gases within the cloud, DENZ assumes that the material is distributed in a Gaussian fashion in the vertical and both horizontal directions (along wind and across wind). The horizontal and vertical coefficients of the Gaussian distributions are functions of the cloud radius and height respectively. For further details of DENZ, the reader is referred to Appendix A of this report and to the code users' manual (Ref. 3).

In the present application, it was found that DENZ could not be used in its original form since it only provides an output of the downwind area which would experience concentrations above a specified hazardous level, regardless of the time after the initial release when such concentrations would occur. Furthermore, it does not calculate the mass of the cloud and does not provide the cloud temperature in the output. These were considered to be major deficiencies in light of the requirements of the designers of the experiments on H2S detonability. It was therefore necessary to develop a new subroutine to operate interactively with DENZ and provide the following outputs at each of the downwind grid points used in DENZ, i.e., at certain time and distance increments:

a) the radius of the cloud at ground level, defined as the point at which the concentration of H2S falls below a specified level.

b) the mass of the cloud, as defined above

c) the volume of the cloud

d) the mass of H2S within the cloud, and

e) the temperature of the cloud

The subroutine was designed to give these outputs for up to ten specified concentration levels in each run. As in the DENZ code, the Gaussian cloud or "puff" idealization was used in the determination of the required parameters. Details of the calculations are given in Appendix B to this report. It should be noted that the Gaussian coefficients used at a given grid point were those derived within DENZ. The cloud temperature, which is carried internally in the main program, was also extracted and printed out by the subroutine.

When running DENZ the user must specify the mass of the hazardous gas released, the mass of air initially mixed with it, as well as the initial temperature and density of the cloud. It can be shown that the latter two parameters are functions of the mass ratio of air to gas and the fraction of the total mass of the gas in liquid phase in the storage tank. These functions were derived in earlier work (Ref. 1) for H2S, assuming the total mass is initially in the liquid phase at 28 degrees C (saturation temperature in the storage tank) and assuming mixing with dry ambient air at a temperature of 0 degrees C. The initial cloud temperatures and densities were calculated on this basis for the selected air/gas mixing ratios.

Four sizes of release were chosen for this study, ranging from 40 tonnes (approximately the capacity of a rail tank car), to 180 tonnes (the capacity of a liquid H2S storage tank at the Bruce heavy water plant). Two intermediate sizes of 90 and 130 tonnes were also chosen. For each release size, the dispersion code was run for three air/gas mixing ratios (10:1, 5:1 and 2:1). Although there is considerable uncertainty concerning the ratio which would be achieved in practice, experimental evidence suggests that a ratio of 10:1 is possible (see discussion

in Ref. 1), although this could well be lower for the larger releases considered here. Accordingly, two lower ratios were selected to test the sensitivity of the dispersion analysis to this factor. The third critical input parameter was the wind speed. Each release size and mixing ratio combination was run with three wind speeds (2, 4 and 8 m/s). At the Bruce heavy water plant site these correspond approximately to the 20, 50 and 90 percentile levels of the wind speed frequency distribution, respectively.

Table 1 summarizes the major variables used in this part of the study and the other user specified input parameters and assumptions used in running DENZ.

## 2. Pipe Breaks

The behaviour of the discharge of H2S vapour from a pipe break has been discussed in detail in an earlier report for the AECB (Ref. 4). It was concluded that the jet of H2S emerges initially at the sound speed of H2S, approximately 290 m/s, and rapidly reaches ambient pressure and temperature after the shock waves formed at the break. Due to the rapid and vigorous mixing in the jet, there would be no significant gravitational effects as a result of the density of H2S.

A simple "top-hat" model was proposed in Ref. 4 to describe the jet behaviour in which the velocity of the jet decreases and the width of the jet increases in direct proportion to distance from the break. An entrainment constant (the constant of proportionality of jet width to downwind distance) of 0.2 was suggested, based on experimental evidence (Ref. 5). Adopting this model for the purposes of the present study, it can be shown that the concentration of H2S in the jet also falls off in direct proportion to

the distance from the break and the distance ($x_c$) from the break required to reach a given concentration (C% by volume) is given by:

$$x_c = \frac{D}{0.2}\left(\frac{100}{C} - 1\right) \qquad (1)$$

where D is the break diameter. It is assumed that the concentration of H2S at the break is 100%. The width of the cloud at $x_c$ is given by:

$$b_c = D + 0.2\, x_c \qquad (2)$$

Equations (1) and (2) were used to estimate the distances to the point where the concentration falls below the ten levels specified for the storage tank rupture studies, together with the jet width at these distances. The analysis was carried out for four pipe break diameters of 50 mm (2"), 150 mm (6"), 600 mm (24") and 1300 mm (52").

## C. RESULTS & DISCUSSION

### 1. Storage Tank Ruptures

The complete output from the 36 runs of the modified DENZ code has been downloaded to six .5¼" floppy disks suitable for detailed examination using any IBM-PC compatible microcomputer system. There are ten data files per run, corresponding to the ten specified concentration levels which define the extent of the cloud. Each file consists of a tabulation of the cloud radius, volume, mass and temperature and the mass of H2S within the cloud as functions of distance and time from the initial release. The data are arranged so that selected functions within a given run can be easily extracted and displayed graphically using a spreadsheet program, such as LOTUS 1-2-3.

Due to the sheer size of the output data, detailed results from only one run are shown here to illustrate the general behaviour of the various functions of interest (Figures 1

and 2). In addition, some characteristic parameters of a flammable cloud having concentrations of H2S above 4% by volume are summarized in Table 2. The characteristic parameters are the maximum cloud radius, volume and mass and the distance and time from release over which the flammable cloud persists.

Figures 1 and 2 show flammable cloud radius, mass, volume and temperature as functions of distance and time respectively for the release of 180 tonnes of H2S with an initial air/gas mixing ratio of 5:1 and a wind speed of 4 m/s. The flammable cloud is defined by the 4% concentration level. The figures illustrate the following general characteristics of the functions, which were generally repeated in all runs:

a) cloud radius increases relatively rapidly, reaching a peak value (in this case at about 300 m downwind) and then diminishing at about the same rate to zero. (It should be noted that the radius versus distance function represents one half of the symmetrical 4% concentration isopleth.)

b) cloud mass and volume are initially fairly constant and then increase to a peak at about the same point as the radius reaches its peak (within one model increment, or about 100m); they then fall off quite rapidly to zero.

c) the percentage increase in mass and volume of the cloud between the point of initial release and the point where these parameters reach their peak is much less than the percentage increase in cloud radius.

d) cloud temperature is still increasing (to the assumed ambient temperature of 273K) when its radius falls to zero indicating that the flammable cloud does not extend into the passive phase.

Figure 3 shows the effect on the function of cloud radius versus downwind distance of varying the specified concentration level defining the edge of the cloud. As expected, the radius of the cloud decreases as the specified concentration increases. However, the downwind extent of the cloud appears to be more sensitive to specified concentration than does the maximum cloud radius.

Examination of Table 2 shows other sensitivities, or lack of sensitivities, of the parameters of the flammable cloud (lower flammability limit 4% by volume) as follows:

a) the maximum cloud radius increases significantly with increasing release size and decreasing wind speed; however, this dependent variable is much less sensitive to the initial air/gas mixing ratio, particularly for the smaller release sizes and higher wind speed cases.

b) the maximum mass and volume of the cloud are quite insensitive to initial air/gas mixing ratio and wind speed, but are approximately proportional to the release size.

c) the time the flammable cloud persists appears to be quite sensitive to wind speed, but comparatively insensitive to air/gas mixing ratio and release size.

d) the distance the flammable cloud persists downwind is much less sensitive to wind speed than is the persistence time. However, it is somewhat more sensitive to release size and air/gas mixing ratio, particularly for the smaller release sizes.

It will be noted that, according to the DENZ model, H2S is distributed in a Gaussion fashion within the cloud. As noted by the original authors of the code (Ref. 3), this is

not consistant with the model of cloud slumping used, in which there is uniform mixing within the cloud. The authors point out that "to within the accuracy expected of the model, it is not an unreasonable assumption". Further inaccuracies may be introduced, however, due to the initial assumptions about the cloud configuration. It is assumed to be cylindrical, with its height equal to its diameter. This is unlikely to be precisely true in a real situation. Furthermore, other important assumptions, such as the rate of entrainment of ambient air, must be made in running DENZ. Fryer and Kaiser (Ref. 3) have noted that the treatment of air entrainment is the single most important difference between the various models available. However, the entrainment model used in DENZ is based on experiments involving the injection of a lighter fluid over a heavier fluid and is supported by some full scale tests with LNG vapour. The slumping formula has apparently been proven by an experiment involving the release of Freon-12 and by the observed consequences of accidental releases of ammonia. Fryer and Kaiser discuss these potential inaccuracies and the general validity of their model in greater detail in Ref. 3.

Recently, McQuaid (Ref. 6) reviewed a study of the performance of 14 heavy gas models, including DENZ, in relation to data collected in the Thorney Island experiments. Performance was evaluated based on concentration versus distance from the point of release and the sensitivity to controlling variables, such as the mass of gas released and the wind speed. The results of this study are not yet available, although another recent study cited by McQuaid indicates that DENZ performs similarly to a wide range of other models presently available.

In addition to the above considerations, a number of uncertainties exist concerning the initial behaviour of a release of H2S. Although DENZ represents the release as instantaneous, H2S would probably be released over a finite time period, even in the event of a catastrophic tank failure. If, as is postulated here, sufficient air cannot be entrained to completely evaporate the tank contents upon failure, this would also extend the period of release as evaporation gradually occurs from suspended droplets or pools of liquid H2S. These effects would probably reduce the downwind and crosswind extents of the flammable cloud but may also increase the time period of a potential hazard.

2. Pipe Breaks

Table 3 gives the estimated distances required for the concentration of H2S in the jet to fall below the specified levels, together with the corresponding widths of the jet at these distances.

It should be noted that the quoted distances and plume widths corresponding to concentrations of 5% or less are likely to be overestimates, since these are about 100 pipe diameters or greater and the jets should be well dissipated at such distances. In practice, under most conditions, atmospheric turbulence would then be the predominant mixing mechanism, resulting in a significantly more dispersed plume of H2S.

## D. CONCLUSION

This report has provided the results of 36 computer simulations of the initial dispersion of H2S released from the catastrophic failure of a storage tank or tank car. The cloud of H2S vapour mixed with ambient air is initially heavier than air and is simulated using the DENZ computer code. This code has been modified to provide the outputs which are needed in the design of experimental studies of the detonability of such H2S releases. These outputs are the mass of H2S in the cloud, the mass and volume of the cloud, its radius at ground level and its temperature, all as functions of distance and time from release. Sample plots of these functions have been given. Characteristic parameters of the functions for a flammable cloud (concentrations of H2S above 4% by volume) have also been given for all 36 simulations. Although these results have shown certain sensitivities and insensitivities of the computer model to the input variables, none of these appear to be inconsistent with intuitive expectations of the cloud behaviour. It was also found that the flammable cloud is always denser than air and does not extend into the passive phase. Thus, its behaviour is not dependent on meteorological variables other than the wind speed. In view of the potential inaccuracies in the model, it is suggested that the results be treated with caution, especially for small distances from the point of release. In the second part of the study, the lengths and widths of jets which would results from breaks in pipes carrying H2S under pressure have been estimated. The length of jet is defined as the distance required from the point of release for the concentration of H2S to fall below a specified level. In most cases, the lengths are of the order of tens of metres only, except for the largest break size (diameter 1300 mm) and lowest specified concentrations (6% H2S by volume, or less). However, it is pointed out that distances and widths calculated for concentrations of 5% or lower are likely to be over estimated.

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Major Variables

Mass of $H_2S$ released (mg*): 40, 90, 130, 180 (tonne)

Air/gas mixing ratio: 10:1 (Initial cloud temperature (T) and density ($\rho$) - 228K, 1,57 kg/m$^3$)

5:1 (Initial cloud temperature (T) and density ($\rho$) - 191K, 1.90 kg/m$^3$)

2:1 (Initial cloud temperature (T) and density ($\rho$) - 108K, 3.45 kg/m$^3$)

Wind Speed (m/s): 2, 4, 8

Concentration level defining edge of cloud (% $H_2S$ by volume): 3, 4, 5, 6, 8, 10, 15, 20, 30, 40

Other Input Parameters and Assumptions

Heating by entrainment at cloud top only ($\alpha^* = 0$, $a' = 0.5$)
No cloud heating by ground or sun.

Input wind speeds assumed to be measured at height of 10m

Ambient temperature (Ta): 273K

Atmospheric stability class: D

Specific heat at constant pressure, air (Cpa): 1011 J/kg/K

Specific heat at constant pressure, $H_2S$ (Cpg): 979 J/kg/K

Density of $H_2S$ at ambient conditions: 1.539 kg/m$^3$

Denisty of ambient air ($\rho a$): 1.29 kg/m$^3$

Surface roughness length: 10 cm

Constant K (Eqn. A3): 1.0

*Note: nomenclature defined and used in equations in Appendix A

TABLE 1: INPUTS TO THE MODIFIED DENZ CODE

| RUN # | SIZE (t) | AIR/GAS RATIO | WIND (m/s) | MAXM RADIUS (m) | MAXM DISTANCE[1] (m) | MAXM TIME[2] (s) | MAXM MASS OF CLOUD (kg) | MAXM VOLUME OF CLOUD ($m^3$) |
|---|---|---|---|---|---|---|---|---|
| 1 | 180 | 10 | 2 | 612 | 486 | 468. | $1.40 \times 10^6$ | $1.00 \times 10^6$ |
| 2 | | | 4 | 406 | 644 | 231 | $1.43 \times 10^6$ | $1.00 \times 10^6$ |
| 3 | | | 8 | 267 | 644 | 93. | $1.43 \times 10^6$ | $1.00 \times 10^6$ |
| 4 | 180 | 5 | 2 | 703 | 486 | 599 | $1.43 \times 10^6$ | $9.92 \times 10^5$ |
| 5 | | | 4 | 466 | 486 | 216 | $1.35 \times 10^6$ | $1.01 \times 10^6$ |
| 6 | | | 8 | 307 | 644 | 107 | $1.43 \times 10^6$ | $9.75 \times 10^5$ |
| 7 | 180 | 2 | 2 | 789 | 277 | 595 | $1.41 \times 10^6$ | $1.01 \times 10^6$ |
| 8 | | | 4 | 534 | 367 | 234 | $1.42 \times 10^6$ | $1.01 \times 10^6$ |
| 9 | | | 8 | 353 | 486 | 105 | $1.41 \times 10^6$ | $1.00 \times 10^6$ |
| 10 | 130 | 10 | 2 | 539 | 486 | 482 | $1.04 \times 10^6$ | $7.19 \times 10^5$ |
| 11 | | | 4 | 353 | 486 | 179 | $1.03 \times 10^6$ | $7.23 \times 10^5$ |
| 12 | | | 8 | 234 | 486 | 71.4 | $1.03 \times 10^6$ | $7.27 \times 10^5$ |
| 13 | 130 | 5 | 2 | 626 | 367 | 486 | $9.99 \times 10^5$ | $7.18 \times 10^5$ |
| 14 | | | 4 | 412 | 486 | 217 | $1.02 \times 10^6$ | $7.00 \times 10^5$ |
| 15 | | | 8 | 270 | 486 | 83.9 | $1.03 \times 10^6$ | $7.27 \times 10^5$ |
| 16 | 130 | 2 | 2 | 694 | 209 | 519 | $1.03 \times 10^6$ | $7.28 \times 10^5$ |
| 17 | | | 4 | 474 | 367 | 231 | $1.03 \times 10^6$ | $6.98 \times 10^5$ |
| 18 | | | 8 | 312 | 486 | 104 | $1.03 \times 10^6$ | $7.00 \times 10^5$ |
| 19 | 90 | 10 | 2 | 466 | 367 | 375 | $7.1 \times 10^5$ | $5.02 \times 10^5$ |
| 20 | | | 4 | 307 | 486 | 183 | $7.17 \times 10^5$ | $5.00 \times 10^5$ |
| 21 | | | 8 | 202 | 486 | 72.9 | $7.17 \times 10^5$ | $4.99 \times 10^5$ |
| 22 | 90 | 5 | 2 | 532 | 367 | 488 | $7.17 \times 10^5$ | $4.98 \times 10^5$ |
| 23 | | | 4 | 352 | 367 | 172 | $7.17 \times 10^5$ | $5.02 \times 10^5$ |
| 24 | | | 8 | 233 | 486 | 84.4 | $7.10 \times 10^5$ | $4.81 \times 10^5$ |
| 25 | 90 | 2 | 2 | 619 | 209 | 488 | $7.08 \times 10^5$ | $5.00 \times 10^5$ |
| 26 | | | 4 | 406 | 277 | 191 | $7.08 \times 10^5$ | $5.03 \times 10^5$ |
| 27 | | | 8 | 267 | 367 | 84.3 | $7.07 \times 10^5$ | $5.03 \times 10^5$ |
| 28 | 40 | 10 | 2 | 334 | 277 | 307 | $3.16 \times 10^5$ | $2.21 \times 10^5$ |
| 29 | | | 4 | 223 | 367 | 146 | $3.19 \times 10^5$ | $2.23 \times 10^5$ |
| 30 | | | 8 | 146 | 367 | 57.6 | $3.19 \times 10^5$ | $2.22 \times 10^5$ |

**TABLE 2**

**CHARACTERISTIC FLAMMABLE CLOUD PARAMETERS FOR EACH RUN OF THE MODIFIED DENZ CODE (CLOUD EDGE DEFINED BY 4% $H_2S$ BY VOLUME)**

| RUN # | SIZE (t) | AIR/GAS RATIO | WIND (m/s) | MAXM RADIUS (m) | MAXM DISTANCE[1] (m) | MAXM TIME[2] (s) | MAXM MASS OF CLOUD (kg) | MAXM VOLUME OF CLOUD ($m^3$) |
|---|---|---|---|---|---|---|---|---|
| 31 | 40 | 5 | 2 | 386 | 209 | 326 | $3.16 \times 10^5$ | $2.24 \times 10^5$ |
| 32 | | | 4 | 256 | 277 | 139 | $3.16 \times 10^5$ | $2.24 \times 10^5$ |
| 33 | | | 8 | 168 | 367 | 670 | $3.17 \times 10^5$ | $2.16 \times 10^5$ |
| 34 | 40 | 2 | 2 | 365 | 119 | 3150 | $2.81 \times 10^5$ | $2.18 \times 10^5$ |
| 35 | | | 4 | 296 | 209 | 156 | $3.13 \times 10^5$ | $2.18 \times 10^5$ |
| 36 | | | 8 | 194 | 277 | 67.5 | $3.09 \times 10^5$ | $2.22 \times 10^5$ |

TABLE 2 (CONT'D)

Notes:

[1] Represents the last DENZ model distance increment at which a non-zero cloud radius was calculated.

[2] Represents the last DENZ model time increment at which a non-zero cloud radius was calculated.

| Concentration of H2S (% by volume) | PIPE BREAK DIAMETER | | | |
|---|---|---|---|---|
| | 50 mm (2") | 150 mm (6") | 600 mm (24") | 1300 mm (52") |
| 3 | 8.08<br>(1.67) | 24.3<br>(5.01) | 97.0<br>(20.0) | 210<br>(43.3) |
| 4 | 6.00<br>(1.25) | 18.0<br>(3.75) | 72.0<br>(15.0) | 156<br>(32.5) |
| 5 | 4.75<br>(1.00) | 14.3<br>(3.01) | 57.0<br>(12.0) | 124<br>(26.1) |
| 6 | 3.92<br>(0.834) | 11.8<br>(2.51) | 47.0<br>(10.0) | 102<br>(21.7) |
| 8 | 2.88<br>(0.626) | 8.63<br>(1.88) | 34.5<br>(7.50) | 74.8<br>(16.3) |
| 10 | 2.25<br>(0.500) | 6.75<br>(1.50) | 27.0<br>(6.00) | 58.5<br>(13.0) |
| 15 | 1.42<br>(0.334) | 4.25<br>(1.00) | 17.0<br>(4.00) | 36.8<br>(8.66) |
| 20 | 1.00<br>(0.250) | 3.00<br>(0.750) | 12.0<br>(3.00) | 26.0<br>(6.50) |
| 30 | 0.583<br>(0.167) | 1.75<br>(0.50) | 7.00<br>(2.00) | 15.2<br>(4.34) |
| 40 | 0.375<br>(0.125) | 1.13<br>(0.376) | 4.50<br>(1.50) | 9.75<br>(3.25) |

**TABLE 3**

**DISTANCES (m) TO CONCENTRATION LEVELS IN JETS FROM PIPE BREAKS (WITH CORRESPONDING JET WIDTHS (m))**

FIGURE 1

CLOUD PARAMETERS VERSUS DISTANCE FROM INITIAL RELEASE

(180 tonnes H2S, Air/Gas Ratio 5:1, Wind Speed 4m/s, Cloud Edge Defined by 4% H2S by Volume)

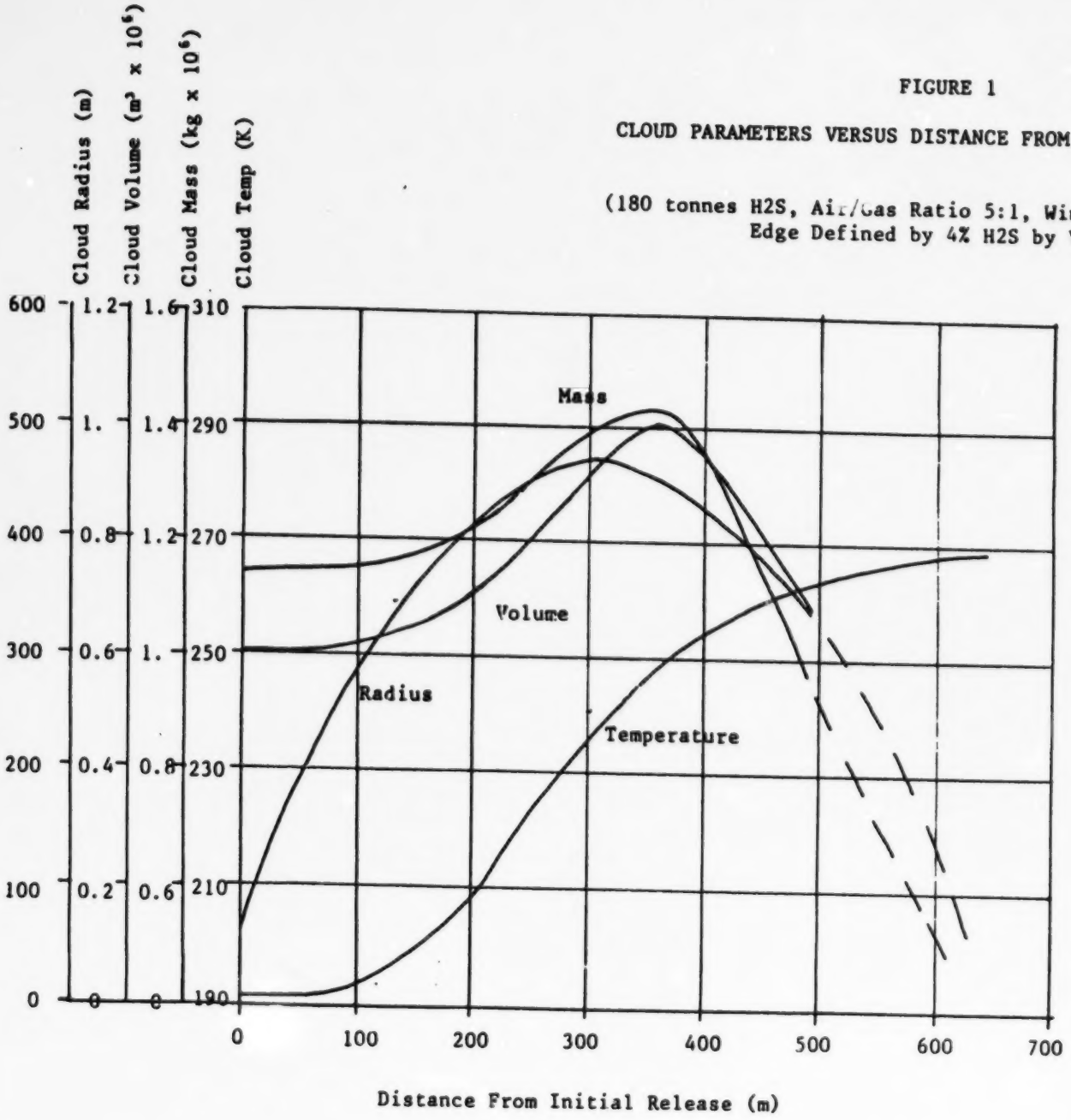


FIGURE 2

CLOUD PARAMETERS VERSUS TIME FROM INITIAL RELEASE

(180 tonnes H2S, Air/Gas Ratio 5:1, Wind Speed 4m/s, Cloud Edge Defined by 4% H2S By Volume)

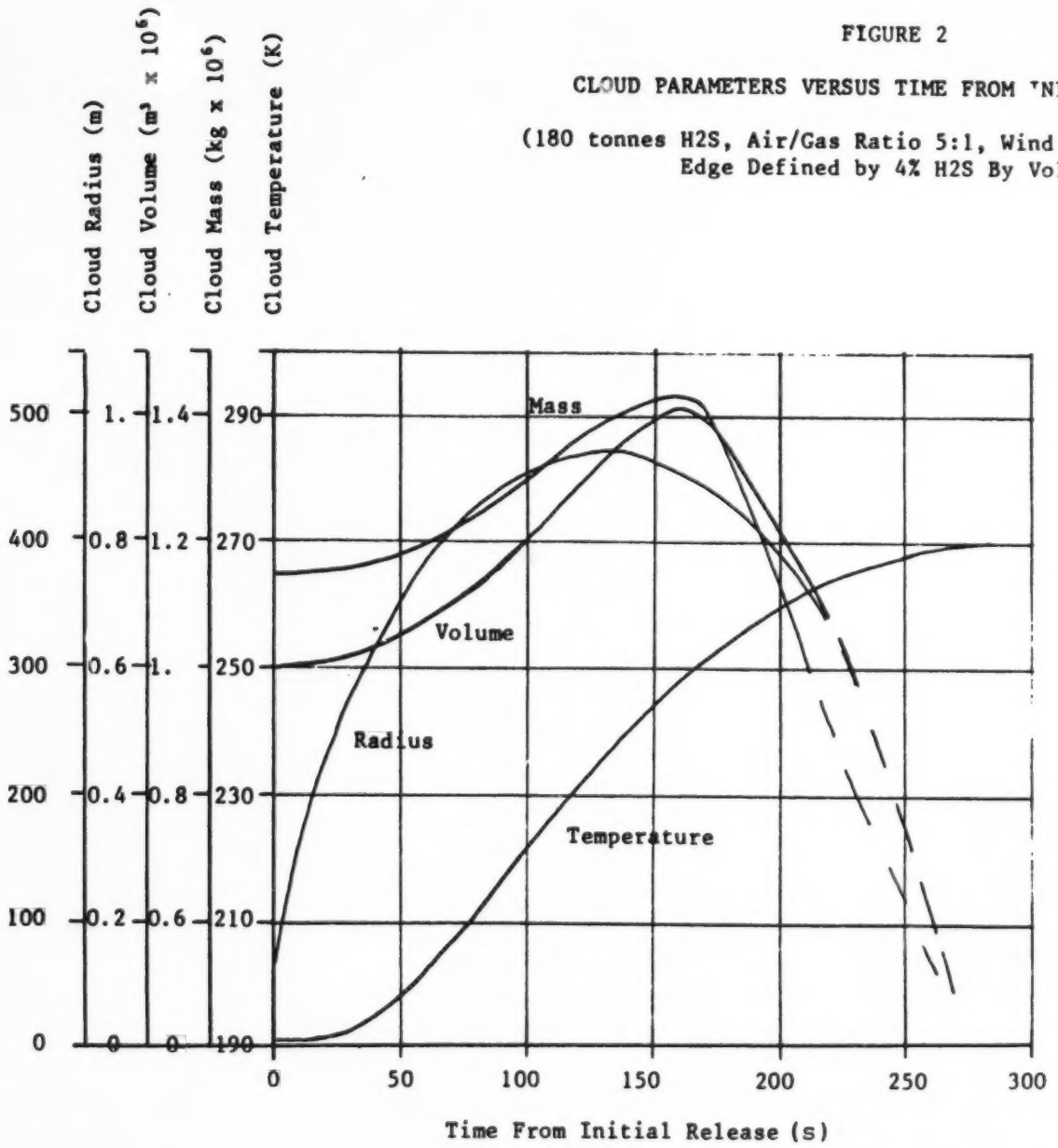
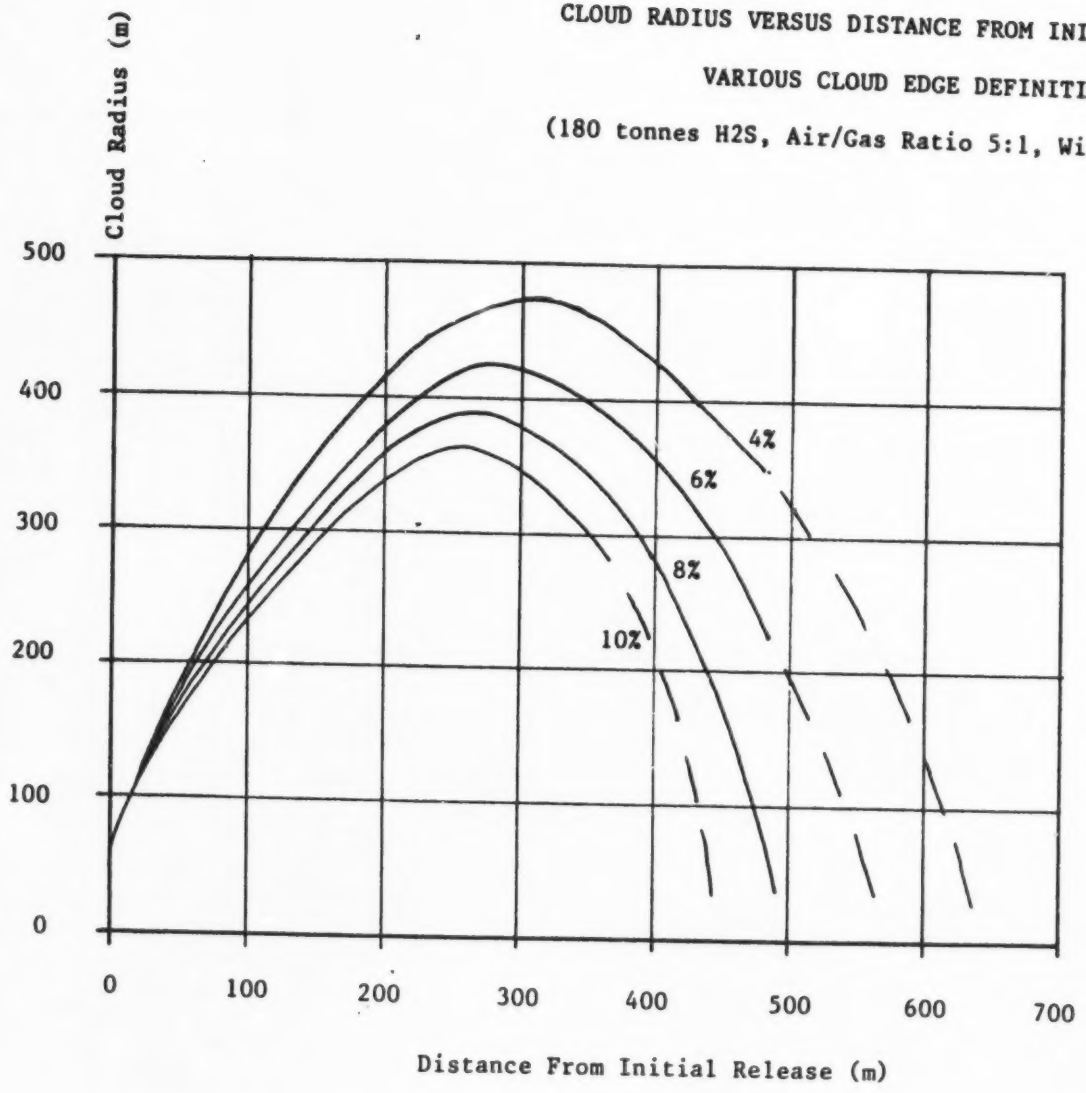


FIGURE 3

CLOUD RADIUS VERSUS DISTANCE FROM INITIAL RELEASE FOR VARIOUS CLOUD EDGE DEFINITIONS

(180 tonnes H2S, Air/Gas Ratio 5:1, Wind Speed 4 m/s)



# APPENDIX A

# SUMMARY OF THE DENZ

# MATHEMATICAL MODEL

The following summary is based on material presented in the DENZ users' manual (Ref. 3).

DENZ assumes that the vapour cloud is initially in the form of a cylinder which then undergoes slumping (following a liquid column analogy), heating by the sun and by contact with ground, and entrainment of ambient air.

The three basic equations governing these processes are as follows:

The rate at which air is entrained into the cloud is given by

$$\frac{dm_a}{dt} = \rho_a(\pi R^2)U_e + 2\rho_a \pi R h \alpha^* \frac{dR}{dt} \qquad (A1)$$

where $m_a$ is the mass of air

$t$ is the time after release

$\rho_a$ is the density of ambient air

$R$ is the radius of the cloud

$U_e$ is the entrainment velocity at the top of the cloud

$h$ is the height of the cloud

$\alpha^*$ is an empirical edge entrainment constant

In this study, the DENZ default values for $\alpha^*$ (0.0) and $U_e$ were used. $U_e$ is dependent on surface roughness (default roughness length 10cm), wind speed, atmospheric stability, the density of the cloud with respect to the ambient air density, and a top entrainment constant (0.5).

The rate of increase of temperature of the cloud is given by:

$$\frac{dT}{dt} = \frac{\frac{dm_a}{dt} C_{pa} \Delta T_a + \alpha(\pi R^2)\Delta T_g^{4/3}}{m_a C_{pa} + m_g C_{pg}}$$

where T is the cloud temperature

$C_{pa}$ is the specific heat at constant pressure of the ambient air

$\Delta T_a$ is the difference in temperature between the air and the cloud

$\Delta T_g$ is the difference in temperature between the ground and the cloud

$m_g$ is the mass of the gas released (H2S in this case)

$C_{pg}$ is the specific heat at constant pressure of the gas released

In this study, ground heating was neglected ($\Delta T_g = 0$)

The rate of increase of the cloud radius is given by:

$$\frac{dR^2}{dt} = 2K \sqrt{\frac{g(\rho-\rho_a)V}{\pi\rho_a}} \qquad \text{(A3)}$$

where K is a constant (taken as unity)

$\rho$ is the density of the cloud

V is the cloud volume

DENZ solves the above equations numerically.

Transition to a passive cloud is determined if the rate of increase of the cloud radius is greater than that expected by atmospheric turbulence alone and the cloud top entrainment velocity is greater than the longitudinal turbulence velocity. Meanwhile, the density difference between the cloud and the ambient air is checked and, if this is less than 0.001 kg/m$^3$, the cloud is assumed passive, even if the above two conditions are not satisfied.

Beyond the point of transition to a passive cloud, DENZ uses a normal Gaussian puff model to describe the dispersion, with initial dispersion coefficients at the time of transition(t) given by

$$\sigma_{zt} = h_t/2.14 \qquad \text{(A4)}$$

$$\sigma_{xt} = \sigma_{yt} = R_t/2.14 \qquad \text{(A5)}$$

where $h_t$ is the cloud height at transition, and

$R_t$ is the cloud radius at transition.

The assumption is made in DENZ that the gas is distributed in a Gaussian fashion within the cloud (see equation (B1) of Appendix B).

# APPENDIX B

# CALCULATION OF CLOUD MASS & MASS OF H2S WITHIN CLOUD

1. CLOUD MASS

Consider a Gaussian "puff" model to represent the concentration profile within the cloud. The coefficients of the Gaussian "puff" are functions of downwind distance (x). $\sigma_x(x)$ is the longditudinal (alongwind) coefficient, $\sigma_y(x)$ is the lateral (across wind) coefficient, and $\sigma_z(x)$ is the vertical coefficient. The horizontal cross-section of the cloud is assumed circular, ie., $\sigma_x(x) = \sigma_y(x)$.

The mass of the cloud is calculated in three steps:

a) determine the height of the cloud (as defined by a specified gas concentration) at selected radius increments.
b) determine the volume of a series of annuli corresponding to the radius increments.
c) sum up the volumes of the annuli out to the edge of the cloud and multiply by the average cloud density (from DENZ) to obtain the cloud mass.

The general equation for the concentration (C) within the cloud is as follows:

$$C(x, y, z) = \frac{2\,mq}{(2\pi)^{3/2}\sigma_x(x_0)\ \sigma_y(x_0)\ \sigma_z(x_0)}$$

$$\times\ \exp\left[-\frac{1}{2}\left(\frac{x - x_0}{\sigma_x(x_0)}\right)^2\right] \quad \times \quad \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y(x_0)}\right)^2\right]$$

$$\times\ \exp\left[-\frac{1}{2}\left(\frac{z}{\sigma_z(x_0)}\right)^2\right] \qquad \text{(B1)}$$

where mg is the mass of gas (H2S) released, (x, y, z) are the co-ordinates of a point in the cloud, relative to the initial point of release, and $x_0$ is the location of the cloud centre.

The height of the cloud at a given radius, or value of $(x - x_0)$, is determined by setting $y = 0$ in eqn.(B1), specifying C and solving for $z(x - x_0)$.

The volume of the annulus is then simply given by

$$V = \pi (x_j^2 - x_i^2) z \qquad \text{(B2)}$$

where $x_i$ and $x_j$ correspond to the mid points between successive radius increments.

2. Mass of H2S in Cloud

The mass of H2S within the cloud is calculated by determining the mass of H2S within each annulus and summing up the resulting values for all annuli.

Firstly, equation (B1) can be simplified to determine the concentration at ground level ($z = 0$), as follows:

$$C_0(x, y, 0) = \frac{2\,mg}{(2\pi)^{2/3}\,\sigma_x(x_0)\sigma_y(x_0)\sigma_z(x_0)}$$

$$\times \exp\left[-\frac{1}{2}\left(\frac{x - x_0}{\sigma_x(x_0)}\right)^2\right] \times \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y(x_0)}\right)^2\right] \qquad \text{(B3)}$$

At a given radius $(x - x_0)$, it can be shown that the vertically averaged concentration $(\bar{C})$ in the cloud is given by:

$$\frac{\bar{C}}{C_0} = \frac{2\sigma_z^2(x_0)}{\sigma_x(x_0)} \left\{1 - e^{\frac{z'^2}{2\sigma_z^2(x_0)}}\right\} \qquad \text{(B4)}$$

where $z'$ is the height of the cloud at the specified radius.

The mass of H2S in each annulus was calculated by solving for $\bar{C}$ in egn.(B4) and multiplying by the annulus volume from eqn.(B2).